Predictive Modeling for Developing Novel Metallic Glass Alloys

THESIS

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in the Graduate School of The Ohio State University

By

Logan Timothy Ward

Graduate Program in Materials Science and Engineering

The Ohio State University

2012

Master's Examination Committee:

Professor Wolfgang Windl, Advisor

Professor Katharine Flores
Abstract

Metallic glasses are a class of material that have been developed to have many unique and useful properties, but have yet to see major application. The amorphous structure of these metals makes them great candidates for applications that need a material that has high strength and can be formed as easily as plastics. However, as a result of their metastable structure, alloys only form in a limited number of systems. This difficulty in locating feasible alloys frustrates designing alloys for new applications. In this thesis, we propose a series of computational tools based on classical molecular dynamics to accelerate the alloy design process.

The first tool presented is a method to rapidly produce accurate alloy interatomic potentials, which are computationally-efficient approximations of bonding in metals. Previously, in order to run an atomistic simulation of a metal alloy, one either had need to resort to slow *ab initio* calculations, rely on unreliable mixing rules to generate the interatomic potential, or spend a large amount of effort creating a alloy potential. To overcome this, we developed a method to create many-component alloy potentials from a library of binaries created by combining previously-developed elemental potentials and fitting the alloy terms. As we will show, potentials created using this method are superior to those generated using mixing rules and just as accurate in simulating metallic glasses as those made for specific alloys using more time-intensive methods.
Additionally, we have developed a novel tool for predicting how easily an alloy will form a metallic glass. Our method uses a combination of parameters that describe the kinetics and energetic stability of the supercooled liquid. To assess the kinetics, we calculate the fragility of the liquid, which describes how viscosity changes as a function of temperature. To evaluate the relative energetic stability, we determine the fraction of efficiently-packed clusters, which have been argued to be the source of stability in supercooled liquids. First, we assessed the correlation of each of these properties against glass-forming ability in a well-studied system and found that fragility is a better predictor for glass formation. Using that knowledge, we then develop a figure of merit, which was successfully used to identify the best glass forming compositions in the Cu-Zr binary and Cu-Zr-Ti ternary systems.

In the third part of this work, we demonstrate a tool for locating alloys with an optimal set of physical properties. To accomplish this, we have developed a tool that uses optimization algorithms to virtually design an alloy without experimental input, which required our method for rapidly generating interatomic potentials. Using this tool, we identified Ni$_{66.4}$Nb$_{21.4}$Al$_{12.2}$ as the ternary metallic glass with the highest elastic modulus in the Ni-Nb-Al-Zr-Ti-Ta system. Also, we predict Ti$_{70}$Ni$_{30}$ to be the metallic glass with the a high stiffness-to-density in the Ni-Cu-Zr-Ti quaternary with the locally best glass-forming ability, as found using our computational tool. Pending experimental evaluation, this method is a possible way to enable rapid and inexpensive design of novel metallic glasses.
Dedication

This document is dedicated to my family.
Acknowledgments

I would like to thank my advisors for their guidance while I worked on this project. The members of the Windl and Flores research groups have been friendly and helpful coworkers. Anupriya Agrawal, Rohan Mishra, and Oscar Restrepo assisted me greatly with some of the technical aspects of this work. Finally, I would like to acknowledge my collaborators Dan Miracle, Kevin Laws, Peter Tsai, and David Riegner.

This work was funded by the Defense Threat Reduction Agency under Grant No. HDTRA1-11-0047 and by the Air Force Office of Scientific Research under Grant No. FA9550-09-1-0251. Simulations were performed at the Ohio Supercomputer Center (Grant No PAS0072). I would also like to acknowledge support by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program.
Vita

2007......................................................University High School, Orlando, Florida

2011..........................................................B.S. Materials Science and Engineering,

The Ohio State University

2011 to present ........................................Graduate Research Associate,

The Ohio State University

Fields of Study

Major Field: Materials Science and Engineering
Table of Contents

Abstract.................................................................................................................................................. ii

Dedication................................................................................................................................................ iv

Acknowledgments ........................................................................................................................................ v

Vita ............................................................................................................................................................ vi

List of Tables .............................................................................................................................................. ix

List of Figures ............................................................................................................................................ x

Chapter 1: Motivation ............................................................................................................................... 1

Background .............................................................................................................................................. 3

Chapter 2: Rapid Development of Alloy Potentials ................................................................................ 6

Introduction ............................................................................................................................................. 6

Method .................................................................................................................................................... 9

Validation ............................................................................................................................................... 14

Advantages and Limitations of the Method ......................................................................................... 30

Conclusions .......................................................................................................................................... 31

Chapter 3: Predicting Glass-Forming Ability ....................................................................................... 32

Introduction .......................................................................................................................................... 32
List of Tables

Table 1: Comparison of mixing enthalpy, bulk modulus, and lattice constant for fcc-Ni, L12-Ni3Al, B2-NiAl, L12-Al3Ni, and fcc-Al in the Ni-Al system; and fcc-Cu, L12-Cu3Au, B2-CuAu, L12Au3Cu, and fcc-Au, calculated using DFT within GGA and EAM potentials fitted in the current work in comparison with experimental data. .......................... 16

Table 2: Mixing enthalpy, bulk modulus, and lattice parameter for all 18 possible B1, B2, L10, L12, and L21 intermetallics in the Cu-Zr-Al system calculated using DFT and potentials developed in this work, by Sheng52, and Zhou using the Johnson alloy model27. The potentials developed in this work were created by fitting to the DFT properties from the B2 and L12 intermetallics............................................................................................................ 24

Table 3: Elastic and physical properties of a Cu45Zr45Al10 metallic glass predicted using molecular dynamics in comparison to experimental data57. The potentials include one generated in this work, a potential holistically fitted to alloy properties and the force-matching approach52, and a potential developed within the Johnson alloy model27. ....... 29

Table 4: Ni-Cu-Zr-Ti based metallic glasses that were tested by the materials design program with the best stiffness-to-density ratio................................................................. 55

Table 5: Materials that were tested by the materials design program with the best figure of merit. ............................................................................................................................ 59
List of Figures

Figure 1: Average deviation between properties for B2-AlNi, L12-Al3Ni, and L12-Ni3Al intermetallics calculated using corrected *ab initio* and EAM potentials created with several weighting strategies. The average difference between an Al-Ni potential by Pun and Mishin and corrected *ab initio* is shown for comparison.*\(^{42}\) .................................................. 18

Figure 2: Pair functions from potentials for Cu and Au from different authors (a) in original form and (b) after standardization transformations designed to make the minimum of the pair function as close as possible to 4% of the cohesive energy.......... 20

Figure 3: Overall fitness of Cu-Au EAM potential generated in the present work with and without standardization transformations made with a Cu potential from Zhou *et al.*\(^{27}\) and Au potentials from different authors, as indicated.......................................................... 21

Figure 4: Median error in mixing enthalpy, bulk modulus, and lattice parameter in reference to *ab initio* data for Cu-Zr-Al potentials with alloy components fitted in this work, developed by Sheng\(^^{52}\), and potentials created using the Johnson alloy model\(^^{27}\). The intermetallics used in testing include all 18 possible B1, B2, L10, L12, and L21 compounds................................................................................................................. 25

Figure 5: Radial distribution functions of Cu\(_{45}\)Zr\(_{45}\)Al\(_{10}\) metallic glasses at 0 K produced using interatomic potentials developed in this work, by Sheng\(^{52}\), and Zhou using the Johnson alloy model\(^{27}\)........................................................................................................................................ 27
Figure 6: Aluminum distribution in Cu$_{45}$Zr$_{45}$Al$_{10}$ metallic glass at 0 K in 16000-atom models generated by simulating a rapid quench from the liquid state using potentials made by (a) this work, (b) Sheng$^{52}$, and (c) the Johnson alloy model$^{27}$. Sheng’s and our potentials show a uniform distribution of aluminum. In contrast, the Johnson alloy potential predicts a distinct demixing the aluminum, which is not likely for this alloy composition$^{57}$. 

Figure 7: Fragility in the Cu-Zr binary system calculated from molecular dynamics simulations (this work) and experimentally measured$^{79}$. The two data sets are normalized such that the fragility of Cu$_{56}$Zr$_{44}$ is equal to unity to account for the quench rate dependence of the fragility$^{80}$. Error bars represent the standard error of the mean. 

Figure 8: Fraction of all atoms that are the center of an icosahedral cluster or the center of a efficient cluster identified using the Effective Radius Ratio method for the Cu-Zr binary system$^{71}$. Compositions with a higher fraction of these clusters should demonstrate increased stability in the supercooled liquid. Error bars represent the standard error of the mean, and are smaller than the symbols. 

Figure 9: Figure of merit for glass forming ability in Cu-Zr binary system, calculated from the predicted fragility and stable cluster fractions, plotted in comparison with experimentally measured critical casting thicknesses$^{84,85,87-94}$. The predicted glass forming ability is shown in comparison to (a) wedge and (b) rod casting thicknesses separately. The three peaks in our computational figure of merit near Cu$_{62}$Zr$_{38}$, Cu$_{50}$Zr$_{50}$, and Cu$_{46}$Zr$_{54}$ correspond to the three alloys with the highest rod critical casting diameter. The red (dashed) line averages the experimental data points to guide the eye.
Figure 10: Figure of merit for glass forming ability in the (a) \( \text{Cu}_{50}\text{Zr}_{(50-x)}\text{Ti}_x \) and (b) \( \text{Cu}_{60}\text{Zr}_{(40-x)}\text{Ti}_x \) systems, calculated from the predicted fragility and stable cluster fractions. \( \text{Cu}_{50}\text{Zr}_{42.5}\text{Ti}_{7.5} \) exhibits the clear maximum in glass forming ability in the \( \text{Cu}_{50}\text{Zr}_{(50-x)}\text{Ti}_x \) system, which is also observed experimentally\(^9^5\). The highest predicted glass forming ability in the \( \text{Cu}_{60}\text{Zr}_{(40-x)}\text{Ti}_x \) system is found for \( \text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10} \) in agreement with experiment as shown by the vertical dashed line in (b)\(^9^6\).

Figure 11: Glass-forming ability of \( \text{Ti}_{100-x}\text{Ni}_x \) binary metallic glasses calculated using a molecular-dynamics method.

Figure 12: Figure of merit of materials tested in the optimization run in the order they were created. The dashed line indicates the maximum of the materials tested so far. The solid line is the average of the last 10 materials that were tested.
Chapter 1: Motivation

Even though there are still many challenges to overcome before metallic glasses become a commonly-used material, their many unique properties make them excellent choices for a large variety of applications. Metallic glasses, unlike conventional metals, do not feature a uniform, crystalline structure but are instead amorphous. This gives them a remarkable set of attractive properties, such as high yield strength and soft magnetic behavior. For this reason, metallic glasses have been used for decades in high-performance transformer cores and are being considered for applications ranging from wear-resistant machine tool coatings to hard tissue prostheses\(^1\). However, metallic glasses are metastable and not the equilibrium product from solidification. Consequently, there are only a limited number of alloy compositions that will form into the amorphous state even with rapid quenching from the liquid.

Considering their limitations, metallic glasses have advanced quite far since their original discovery in 1960\(^2\). At the time, it was only possible to produce a flake of a Au-Si amorphous alloy 10 μm thick. Since then, the understanding of what allows some alloys to easily bypass crystallization has allowed scientists to produce alloys of increasingly greater thickness. The first of these “bulk metallic glasses” in the Pd-Si-Au ternary were able to be cast in thicknesses of 1 mm, owing to their increased resistance to crystallization\(^3\). Modern metallic glass alloys can be cast in rods of diameters well over
1 cm and exist in many different alloy systems. However, discovering and optimizing a new alloy is still a difficult, time-consuming process.

Designing one of these new metallic glass alloys has typically been accomplished using empirical rules and a significant amount of experimental exploration of a target alloy system. Based on the empirical rules, it is desirable to select an alloy system with a large number of constituents, a large difference in atomic sizes, and negative mixing enthalpies. The science behind these rules is based on the idea that metallic glass feature efficiently-packed, yet non-crystalline, structures that lead to their overall stability. Once these rules are used to find a target alloy system, the best place suggested to search for metallic glasses is near eutectic compositions, where the liquid is particularly stable against crystallization. However, it is difficult to locate eutectics in multicomponent systems and this rule – as we will demonstrate in Chapter 3 – is not very accurate in some cases.

The difficulty in simply locating a metallic glass makes designing an alloy with specific physical properties even more difficult. For that reason, there has been a large focus on developing computational tools to accelerate the search for useful metallic glasses using a wide spread of techniques ranging from computational thermodynamics to molecular dynamics. Of these, the most accurate methods have relied on computational thermodynamics, which requires large, specific experimental databases. And, coupling any of these techniques with a method for predicting whether the alloy will have useful properties has also not been well addressed.
In this work, we present a compilation of computational methods that enable one to develop metallic glasses with minimal experimental input. These tools are based on classical molecular dynamics, which can be used to predict a large number of material properties. We utilize this capability to develop a novel scheme for predicting the best alloys in a system for glass-forming ability (Chapter 3) and with useful physical properties (Chapter 4). To enable the application of these tools to a large number of metallic systems, the work described in this thesis includes a means of rapidly producing interatomic potentials from \textit{ab initio} methods (Chapter 2), which are the sole requirement for predictively modeling a system using molecular dynamics.

Background

\textit{Molecular Dynamics}

Molecular dynamics is based on using classical mechanics to model the evolution of a system of atoms over time. Using statistical mechanics, it is possible to control and measure the system variables such as temperature, pressure, and density. Depending on available processing power and the complexity of the energy calculations, one can model systems with up to billions of atoms on timescales up to a few microseconds. While this method is limited in size and timescale, it does allow one to directly model the influence of atomic structure on properties. In the case of amorphous systems, the lack of any structural features larger than a few nanometers should allow one to model most fundamental processes in systems containing tens of thousands of atoms.

The major differentiating feature between molecular dynamics techniques is the method used to calculate energies. The two main techniques for metals are \textit{ab initio}
techniques, such as Density Functional Theory (DFT)\textsuperscript{14}, and interatomic potentials. DFT determines the energy of a system of atoms by solving its electronic structure, which limits the system size to a relatively small number of atoms (<1000) and very short timescales (<1 ns) due to the computational expense. However, this comes with the major advantage of being able to model systems containing any combination of elements with decent accuracy without any need for experimental input.

The alternative method, using interatomic potentials, calculates the energy of a system using simple functions that do not explicitly consider the electronic structure. These functions, known as interatomic potentials, are tuned to be able to replicate \textit{ab initio} or experimental data for specific compounds. In the simplest case, these functions can be thought of as coarse approximations of bonding in materials, and therefore do not have the versatility of DFT calculations. However, they are substantially faster and allow atomistic simulations to consider millions or more atoms on timescales extending up to 10s and 100s of nanoseconds.

The embedded-atom method (EAM) is a type of interatomic potential that allows for changes in bonding strength around defects, which is necessary for accurately modeling metals\textsuperscript{15}. The EAM calculates the energy of each atom based on the positions of the other atoms through the relation

\[ U_i = F_{\alpha} \left( \sum_{i \neq j} f_{\beta} (r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{\alpha\beta} (r_{ij}) \]  

(1)
which consists of a pair term, $\phi$, and a many body term, $F$, that depends on the contributions to local “electron density” via, $f$. For a single element system, each of these three functions is tuned to reflect properties of the metal.

**Genetic Algorithms**

The ability of genetic algorithms to perform global searches in systems that may contain several local extrema makes them well suited to materials design problems. While there are many similar algorithms that can perform this sort of global optimization, such as simulated annealing\textsuperscript{16}, we chose to focus on this algorithm for our work because they have been shown to be successful and versatile in several previous design studies\textsuperscript{17–21}. The procedure of genetic algorithms can be easily likened to the processes of natural evolution: genes describing individuals in a population pool are mixed and mutated until the best-performing traits are developed. In terms of a computing algorithm, this requires three operations\textsuperscript{21}:

(i) **Selection**: Choosing a subset of individuals for creating a new generation  
(ii) **Crossover**: Mixing two parents to form a new individual  
(iii) **Mutation**: Altering the characteristics of an individual after crossover

Although the specifics of how these operations are designed and implemented can vary greatly depending on the target, the iterative process of selection, crossover, and mutation is identical for any simple genetic algorithm. For our work, we will use an elitist strategy for selection, which ensures the top performing individuals are always in the pool for crossover\textsuperscript{22}. The specifics of the crossover and mutation algorithm for each problem are described in Chapters 2 and 4.
Elements of this chapter were adapted from:


Chapter 2: Rapid Development of Alloy Potentials

Introduction

Classical molecular dynamics (MD) simulations have become ubiquitous tools for simulating complex behavior in many materials systems from atomistic to increasingly larger length scales. One of the key issues limiting the ability for materials scientists to design metallic materials from the atom up using classical MD is the lack of interatomic potentials suitable for the desired alloy system. Interatomic potentials, which approximate complex interatomic interactions using computationally efficient functions, range from simple pair interactions to more complex formulations that involve the local electron density and bond angles. Of these, the embedded-atom method (EAM) has been used widely because of its low computational costs and ability to accurately model bulk properties and defects in metals\textsuperscript{23,24}.

The EAM is a many-body interatomic potential consisting of a pair function and a many-body interaction term. In the Finnis-Sinclair form of the embedded atom method\textsuperscript{24}, the energy of a single atom is computed as

\[
U_i = F_\alpha \left( \sum_{i \neq j} f_{\alpha \beta} (r_{ij}) \right) + \frac{1}{2} \sum_{i \neq j} \phi_{\alpha \beta} (r_{ij})
\]  

(2)
where the sum is over all atoms less than a cutoff distance apart. The key features of this formula are a pair-interaction term, $\phi$, and an embedding function $F$, that depend non-linearly on the contributions from the neighboring atoms to the local electron density, $f$. In this form, the pair-interaction and electron density functions are different for each combination of central atom type ($\alpha$) and neighbor type ($\beta$), whereas the embedding functions are specific to the species of each neighbor, $\beta$, and central atom, $\alpha$, respectively.

Whereas good-quality EAM potentials exist for a considerable number of elemental metals\textsuperscript{25–27}, potentials for alloy systems are sparse and typically require considerable development effort\textsuperscript{28}, which makes fast exploration of new alloy compositions rather difficult. Interatomic potentials describing alloys are often developed by coupling several previously-developed pure element potentials and fitting the cross-interaction functions against experimental or ab initio data from the alloy system (i.e. mixing enthalpies and moduli)\textsuperscript{29,30}. Along with fitting the cross-interaction terms, it is possible to increase the quality of the potential by making alterations to the pure-species functions that effect the calculated alloy energies, but leave pure element energies unaffected\textsuperscript{29}. These alterations to the elemental components are unique to each fitted binary system, which means they must be adjusted when adding additional elements to a potential. This makes the development of many-component alloy potentials slow and limits the accuracy as more components are added, as the same transformations must satisfy even more objectives. If one seeks to mitigate this problem by fitting pure and alloy functions simultaneously, the
number of fitting parameters becomes impractical to optimize for systems with more than 4 or 5 components\textsuperscript{28}.

The Johnson alloy model was proposed with the goal of creating multi-component EAM potentials without significant computational expense\textsuperscript{31}. The basic idea of this method is to generate the new pair functions for dissimilar species (cross-potentials) required to create an alloy potential as electron density-weighted averages of the elemental components based on an empirical model,

\[
\phi_{\alpha\beta}(r) = \frac{1}{2} \left( \frac{f_\beta(r)}{f_\alpha(r)} \phi_{\alpha\alpha}(r) + \frac{f_\alpha(r)}{f_\beta(r)} \phi_{\beta\beta}(r) \right). \tag{3}
\]

It is important to note that this method uses a different version of the EAM in which the electron density function \((f_\alpha)\) is only specific to a single-atom type rather than to a pair of types as in the Finnis-Sinclair EAM potential. In order to ensure the best-possible alloy potentials between many different elements, this method only requires finding compatible magnitudes for the electron density functions of all of the elements in a database and ensuring slope of the embedding function of each potential is zero at the equilibrium electron density for that species. The compatible magnitudes are set by introducing a scaling parameter for each electron density function that, in order to leave the elemental embedding energy unchanged, is compensated for by reciprocal scaling in the embedding function. The appropriate scaling factor can be determined by minimizing the total error in the dilute heats of solution for each possible binary in the database\textsuperscript{31}, or using an empirical relationship based on the cohesive energy and atomic volume of each
constituent\textsuperscript{32,33}. In this work, we will demonstrate that this method, while fast, can significantly compromise the accuracy of interatomic interactions in alloy systems.

The method presented in this paper has computational expenses somewhat higher than those required for the Johnson alloy model, but is considerably more accurate than this model while also being faster than holistic fits encompassing the entire alloy system. We propose creating binary Finnis-Sinclair EAM potentials using high-quality elemental EAM potentials from the literature with only small modifications and cross-potentials components fit to a limited number of properties of a limited set of intermetallic phases calculated from first principles. We show that these binaries can be combined into many-component alloy potentials without significant alteration or additional fitting required, which opens a new path for large-scale exploration of multi-component alloys.

Method

The method proposed in this paper describes a generally applicable method to join elemental EAM potentials and fit the necessary alloy functions to data calculated using Density Functional Theory (DFT).

\textit{Ab Initio Calculations}

In order to generate a training set, the equilibrium lattice parameter, mixing enthalpy, and bulk modulus are calculated using DFT for the B2 and both L1\textsubscript{2} intermetallics in the desired binary. In our implementation of this method, these are calculated using VASP with plane wave basis sets and GGA exchange-correlation\textsuperscript{34–36}. The number of k-points used for each calculation is increased until the total energy changes by less than 0.01%
with the addition of more k-points. Generally, this convergence is reached with a grid of $14 \times 14 \times 14$ k-points.

In order to compensate for the difference between lattice parameters and bulk moduli predicted by DFT and measured experimentally, a simple “rule-of-mixtures” approach is used. For each element, correction factors for the lattice parameters and bulk modulus are determined using

$$C_{\text{lattice}} = \frac{1}{3} \left( \frac{a_{\text{Expt.}}}{a_{\text{DFT}}} + \frac{b_{\text{Expt.}}}{b_{\text{DFT}}} + \frac{c_{\text{Expt.}}}{c_{\text{DFT}}} \right)$$

(4)

$$C_{\text{Modulus}} = \frac{K_{\text{Expt.}}}{K_{\text{DFT}}}$$

(5)

The moduli and lattice parameters calculated for intermetallics are multiplied with an effective correction factor, which is an average of the elemental correction factors weighted by composition. Handbook values are easily available for the experimental data required for these correction factors\textsuperscript{37–39}.

**Potential Fitting Procedure**

The following sub-section outlines methods to combine elemental potentials, fit cross-potential functions against *ab initio* data, and then join binaries into more-complex potentials.

**Standardizing Elemental Potentials**

The single-element potentials are initially adapted to improve compatibility in binary and multicomponent potentials in a way that preserves the original accuracy in the pure systems. First, the embedding functions are adjusted to exist on the same range of
arbitrary units and the electron density functions are scaled appropriately using the invariant transformations\textsuperscript{29}

\[
F(\rho) \rightarrow F\left(\frac{\rho}{s}\right),
\]

\[
f(r) \rightarrow s \cdot f(r).
\]

where \(\rho\) is an electron density, \(s\) is an arbitrary scaling factor, and \(r\) is a distance. Second, the pair interaction functions are adjusted to be of a qualitatively similar form. Depending on the functional form used in the original potentials, these functions can range from repulsive at all distances\textsuperscript{40} to attractive at long distances\textsuperscript{27}. In this work, we chose to transform the potentials into the latter form by adjusting the pair function such that its minimum is 4\% of the cohesive energy using the invariant transformations demonstrated by Voter\textsuperscript{29}

\[
F(\rho) \rightarrow F(\rho) + g \cdot \rho
\]

\[
\phi(r) \rightarrow \phi(r) - 2g \cdot f(r)
\]

where \(g\) is the transfer parameter.

\textbf{Joining Elemental Potentials}

When joining two elemental potentials, the maximum cutoff distance between the two potentials is adopted for the binary potential. The electron density functions and pair interaction terms from the original potentials are defined as equal to 0 for distances greater than the original cutoff. As most interatomic potentials are available in a tabulated format with each function defined on discrete intervals, our implementation uses a cubic
spline interpolation to evaluate each component functions on values not specified in the
original table.

**Fitting Cross-Potentials**

The Finnis-Sinclair formulation for an EAM potential is used for each alloy
potential. For a binary system, this requires two embedding functions \((F_\alpha, F_\beta)\), four
electron density functions \((f_{\alpha\alpha}, f_{\alpha\beta}, f_{\beta\alpha}, f_{\beta\beta})\), and three pair interaction functions \((\phi_{\alpha\alpha}, \phi_{\alpha\beta}, \phi_{\beta\beta})\). Since the functions involving only one atomic species are supplied by the
single-element potentials, it is only necessary to fit three interspecies functions, which are
two electron densities and one pair potential.

We chose to fit the electron density functions as scaled versions of the elemental
functions, where

\[
f_{\alpha\beta}(r) = s_\alpha \cdot f_{\alpha\alpha}(r),
\]

\[
f_{\beta\alpha}(r) = s_\beta \cdot f_{\beta\beta}(r).
\]

This method adjusts the electron density function to compensate for the electron density
cloud around an atom reacting differently depending on the adjacent species. In this form,
we assume that the effective magnitude of the density clouds is different, but not the
shape. The key advantage of this technique is that it only requires two fitting parameters,
\(s_\alpha\) and \(s_\beta\), and does not require knowing the original functional forms of the electron
density functions.

The pair interaction function is fitted using a Morse function, which is defined as
This function was chosen because its shape reflects the standardized pair potential shape specified earlier, which is highly repulsive at short distances and slightly attractive at long distances. The Morse function was chosen in lieu of other functions with this shape because of its simplicity, with only three fitting parameters, $E_1$, $\alpha$, and $r_0$. Each parameter is allowed to vary over any range, with $\alpha > 0.9$ Å$^{-1}$ being the only constraint. This range was chosen based on the observation that $\alpha$ values smaller than approximately 0.9 Å$^{-1}$ lead to unphysical behavior in some of the tested intermetallic compounds.

In order to ensure that the function and its first derivative approach zero at the cutoff distance, the transformation

$$
\phi_{\alpha\beta}(r) = E_1[e^{(-2\alpha(r-r_0))} - 2e^{(-\alpha(r-r_0))}].
$$

(12)

is applied to the pair function$^{41}$. In all of the potentials generated in this study, $m$ was set to 20.

The optimum values of all five coefficients (two for the electron density and three from the pair function) are determined by minimizing the difference between the mixing enthalpy, bulk modulus, and lattice parameters of the B2 and L1$_2$ intermetallics calculated by our potential and corrected DFT. A genetic algorithm was chosen to optimize the objective function, which is the weighted sum of total error in mixing enthalpy, and fractional errors in bulk modulus and lattice parameter calculated using the relationship:
\[
\frac{1}{F} = \sum_i \left[ \frac{\Delta H_{m,i}}{w_H} + \left( \frac{\Delta K_i}{K_{i,DFT}} + w_a \cdot \frac{\Delta a_i}{a_{i,DFT}} \right) \right].
\]

In this form, \( F \) represents the fitness of the potential with respect to matching the corrected \textit{ab initio} values. The weight factors \( w_H, w_K, \) and \( w_a \) were set to be 0.4 eV, 1.0, and 1.6, respectively. The weights for each property were fixed by adjusting each parameter using a balanced approach until differences between the mixing enthalpies, bulk moduli and lattice parameters calculated using our potential and \textit{ab initio} were equivalent to or smaller than those differences from an Al-Ni potential available in the literature\textsuperscript{42}, as described below. These weight factors were subsequently used for every binary potential created in our study.

\textbf{Joining into Many-Component Potentials}

As with the single-component potentials, the binaries are combined by transforming the embedding functions to exist on the same range and adopting the maximum cutoff radius. As long as the same pure element potentials are used to create each binary, the electron density and pair interaction functions contained within the source binaries are sufficient to create higher-order potentials without any additional fitting. In addition, the properties of each binary system and the original pure elements are preserved in these new potentials.

\textbf{Validation}

Potentials created with the proposed technique were validated by comparison with experimental results and existing alloy potentials. In addition, the dependence of the accuracy of our binary potentials on the source of the elemental potentials was assessed.
Comparison to Experimental Values

Potentials were created for the Al-Ni and Cu-Au systems in order to evaluate their ability to replicate experimental data and to ensure DFT is suitable for providing a training set of intermetallic properties. For both systems, elemental potentials from Zhou et al. were used to generate interatomic potentials\(^{27}\) and experimental data was taken from\(^{43-48}\). Elemental potentials from the same author were used to remove author compatibility as a factor for this test.

As shown in Table 1, there is generally good agreement of mixing enthalpy, bulk modulus, and lattice parameter between DFT, the fitted EAM potentials, and experiment. Also, the DFT correction factors to the bulk moduli and lattice parameters from Eq. (4) and (5) were found to be a necessary addition to this method. For example, the bulk modulus of Au\(_3\)Cu calculated with DFT is 26 GPa (16%) below the experimental values without correction and only 1.4% after correction. Overall, the DFT values for mixing enthalpy and the corrected DFT values for bulk modulus and lattice parameter agree exceptionally well with experiment and are all within 0.075 eV, 10 GPa, and 0.03 Å of experimental values, respectively. In contrast, the uncorrected DFT values for bulk modulus and lattice constant deviated as much as 34 GPa and 0.09 Å. Based on this result, it was concluded that corrected DFT is suitable for creating a training set of intermetallic properties.
Table 1: Comparison of mixing enthalpy, bulk modulus, and lattice constant for fcc-Ni, L1_2-Ni_3Al, B2-NiAl, L1_2-Al_3Ni, and fcc-Al in the Ni-Al system; and fcc-Cu, L1_2-Cu_3Au, B2-CuAu, L1_2Au_3Cu, and fcc-Au, calculated using DFT within GGA and EAM potentials fitted in the current work in comparison with experimental data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mixing Enthalpy [eV/atom]</th>
<th>Bulk Modulus [GPa]</th>
<th>Lattice Constant [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EAM</td>
<td>DFT</td>
<td>Experiment</td>
</tr>
<tr>
<td>fcc-Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L1_2-Ni_3Al</td>
<td>-0.445</td>
<td>-0.444</td>
<td>-0.387^a</td>
</tr>
<tr>
<td>B2-NiAl</td>
<td>-0.667</td>
<td>-0.675</td>
<td>-0.609^a</td>
</tr>
<tr>
<td>L1_2-Al_3Ni</td>
<td>-0.238</td>
<td>-0.223</td>
<td>-</td>
</tr>
<tr>
<td>fcc-Al</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>fcc-Cu</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L1_2-Cu_3Au</td>
<td>-0.042</td>
<td>-0.042</td>
<td>-0.070^a</td>
</tr>
<tr>
<td>B2-CuAu</td>
<td>-0.040</td>
<td>-0.049</td>
<td>-</td>
</tr>
<tr>
<td>L1_2-Au_3Cu</td>
<td>-0.023</td>
<td>-0.022</td>
<td>-0.060^b</td>
</tr>
<tr>
<td>fcc-Au</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

^a Ref 43, values at ambient temperature
^b Ref 44 for compound data, Ref 45 for elemental
^c Ref 46
^d Ref 47
^e Ref 48
^f Ref 38
The degree that our potentials agree with corrected DFT was found to be strongly dependent on the weight factors used in Equation 14. As shown in Figure 1, it is possible to reproduce a single property extremely well at the expense of others by weighting that property heavily. Potentials that ignore key material properties are not desirable, so an even balance between them was adopted. To decide on the proper weighting between properties, the weight factors in Equation 14 were adjusted until differences between the mixing enthalpies, bulk moduli and lattice parameters calculated using our potential and ab initio were equivalent to or smaller than those differences from an Al-Ni potential available in the literature\textsuperscript{42}. These weight factors were subsequently used for every binary potential created in our study.

The EAM potentials are able to replicate this training set with only small deviations from the corrected DFT data, as shown in Table 1. In the Al-Ni binary, the maximum error in mixing enthalpy, bulk modulus, and lattice parameter are very low at 0.015 eV, 10 GPa, and 0.07 Å, respectively. The maximum errors compare well to a recent potential developed to model NiAl and Ni$_3$Al intermetallics\textsuperscript{42}, which has maximum errors of 0.17 eV, 29 GPa, and 0.06 Å. The maximum errors for our potential in the Cu-Au system are even lower at 0.009 eV, 7 GPa, and 0.04 Å, respectively. This Cu-Au compares favorably to a potential developed by Zhou et al. using the Johnson alloy model\textsuperscript{27}, which differs as much as 0.07 eV, 43.6 GPa, and 0.04 Å for the same three tested intermetallics. This shows that our method can generate binary potentials that match DFT and experimental properties just as well as, if not better than, other potentials available in literature.
Figure 1: Average deviation between properties for B2-AlNi, L1_2-Al_3Ni, and L1_2-Ni_3Al intermetallics calculated using corrected \textit{ab initio} and EAM potentials created with several weighting strategies. The average difference between an Al-Ni potential by Pun and Mishin and corrected \textit{ab initio} is shown for comparison.\textsuperscript{42}

\textbf{Effect of Potentials from Different Authors}

The Cu-Au binary was refit with elemental potentials for gold from other authors in order to assess the effect of using elemental potentials with a broad sample of potential fitting approaches\textsuperscript{27,49–51}. For instance, the Ackland potential functions are based on fixed forms and fit to the Au lattice parameter, elastic constants, vacancy formation energy, cohesive energy, and the stacking fault energy\textsuperscript{50}. In contrast, the Au potential developed by Sheng used quintic splines fit using the force-matching approach and a large database of properties including phonon frequencies and elastic constants\textsuperscript{51}. Consequently, the
functions generated by each method are quite different even though they are all designed to model the same element, and all yield similar values for the cohesive energy, bulk modulus, and lattice parameter of FCC gold.

The differences in the EAM functions produced are especially visible in the pair interaction components of each potential, shown in Figure 2a. While the potentials from Zhou and Grochola\textsuperscript{27,49} are slightly negative near the FCC equilibrium distance (≈3 Å), the Ackland potential pair term is positive below 3.25 Å and the Sheng potential has a global minimum at 1.5 Å. In order to adjust each potential into a standardized form, an invariant transformation was applied so that the pair function has a minimum equal to 4% of the cohesive energy. This value was chosen to be consistent with other potentials in literature with Morse-like pair functions, such as those by Zhou\textsuperscript{27}, which were found to have minima between 3-5% of the cohesive energy. After applying the standardization transformations, the pair functions from each potential (shown in Figure 2b) are qualitatively similar to a Morse function, with strong repulsion at short distances and weak attraction at higher distances. Assuming that an optimal cross-potential pair function will have a shape similar to the pair functions from the pure element potentials, this transformation should increase the accuracy of the binary alloy potential.
**Figure 2**: Pair functions from potentials for Cu and Au from different authors (a) in original form and (b) after standardization transformations designed to make the minimum of the pair function as close as possible to 4% of the cohesive energy.
Depending on the fraction of the cohesive energy chosen for the minimum of the pair function, the magnitudes of the fitness for each potential were found to change. This is unsurprising given that the transformations used to standardize potentials were originally used as fitting parameters when creating an alloy potential\textsuperscript{29}. However, it would be impractical to use the standardization transformations as fitting tools as it would alter the elemental components differently in each binary potential, thereby preventing the generation of higher-order potentials from a binary database.

![Fitness Comparison Graph]

**Figure 3:** Overall fitness of Cu-Au EAM potential generated in the present work with and without standardization transformations made with a Cu potential from Zhou *et al.*\textsuperscript{27} and Au potentials from different authors, as indicated.

The optimized fitness parameter of each binary potential, calculated using Equation 14, created from each elemental potential in the original and standardized form
is shown in Figure 3. Potential standardization is a key feature of this method as it allows potentials from different authors to be used effectively regardless of their choice of functional form. This is evidenced by the fact that the fitness parameter of the alloy potentials created with a gold potential from Ackland increased from 2.2 to 5.2 after applying the transformation, which makes it competitive as a selection for the gold component of the Cu-Au potential. It was also found that using potentials from the same author for copper and gold yield the best alloy potentials, which is presumably due to the choice of the same functional form for the embedding and election density functions. Even so, the other Cu-Au binary potentials created using the Zhou, Ackland, or Grochola gold potentials have competitively high finesses after the transformation. This further demonstrates that our standardization method considerably lessens the penalty of using potentials from different authors.

It was found that not all elemental potentials are suitable for creating alloy potentials using our method. For instance, the binary potential created using a gold potential developed by Sheng has a notably lower fitness that is worsened by standardization. The incompatibility can be attributed to the strongly different functional form used for the pair potential, with the minimum in the pair function originally two orders of magnitude lower than any other tested gold potential. While it would be impractical to prescribe a standard shape to produce optimal alloy potentials based on our work, it is possible to use our potential fitting method as a simple check to test the feasibility of a new elemental potential for use in generating a library of alloy potentials.

*Comparison with other Alloy Potentials*
To benchmark our proposed method against current literature standards, we have developed a potential describing the Cu-Zr-Al ternary system using elemental potentials from a database developed by Zhou et al. This potential will be compared with the ternary potential generated using identical pure potentials combined using the Johnson alloy model, as originally proposed by the author. It will also be compared with a Cu-Zr-Al potential developed by Sheng et al. with all functions fit simultaneously against an extensive library of crystalline and amorphous structures using the force-matching method.

Accuracy in Modeling Intermetallics

In order to evaluate each potential’s effectiveness in modeling intermetallics, the properties of all possible L1₀, L1₂, L2₁, B1, and B2 structures in the Cu-Zr-Al ternary were first calculated using corrected DFT, as described earlier. In total, the entire testing set contains 9 intermetallics used for fitting our potential (3 B2 and 6 L1₂) and 9 others, including 3 ternary compounds. The properties of those intermetallics were then calculated using all three potentials, with the median errors shown in Figure 4. A complete comparison of the properties calculated by each potential is available in Table 2.
Table 2: Mixing enthalpy, bulk modulus, and lattice parameter for all 18 possible B1, B2, L1₀, L1₂, and L2₁ intermetallics in the Cu-Zr-Al system calculated using DFT and potentials developed in this work, by Sheng²⁷, and Zhou using the Johnson alloy model²⁷. The potentials developed in this work were created by fitting to the DFT properties from the B2 and L1₂ intermetallics.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mixing Enthalpy [eV]</th>
<th>Bulk Modulus [GPa]</th>
<th>Lattice Parameter [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>This Work</td>
<td>Sheng²⁷</td>
</tr>
<tr>
<td>B2-AlCu</td>
<td>-0.139</td>
<td>-0.140</td>
<td>-0.293</td>
</tr>
<tr>
<td>B2-AlZr</td>
<td>-0.318</td>
<td>-0.449</td>
<td>-0.397</td>
</tr>
<tr>
<td>B2-CuZr</td>
<td>-0.138</td>
<td>-0.043</td>
<td>-0.137</td>
</tr>
<tr>
<td>L₁₂-Al₃Cu</td>
<td>-0.040</td>
<td>-0.043</td>
<td>-0.111</td>
</tr>
<tr>
<td>L₁₂-Al₁Zr</td>
<td>-0.475</td>
<td>-0.446</td>
<td>-0.348</td>
</tr>
<tr>
<td>L₁₂-Cu₃Al</td>
<td>-0.177</td>
<td>-0.101</td>
<td>-0.237</td>
</tr>
<tr>
<td>L₁₂-Cu₃Zr</td>
<td>0.110</td>
<td>0.107</td>
<td>-0.023</td>
</tr>
<tr>
<td>L₁₂-Zr₂Al</td>
<td>-0.342</td>
<td>-0.332</td>
<td>-0.265</td>
</tr>
<tr>
<td>L₁₂-Zr₂Cu</td>
<td>-0.012</td>
<td>-0.012</td>
<td>0.056</td>
</tr>
<tr>
<td>B₁-AlCu</td>
<td>0.193</td>
<td>0.229</td>
<td>-0.004</td>
</tr>
<tr>
<td>B₁-AlZr</td>
<td>-0.023</td>
<td>-0.449</td>
<td>-0.066</td>
</tr>
<tr>
<td>B₁-CuZr</td>
<td>0.228</td>
<td>0.504</td>
<td>0.150</td>
</tr>
<tr>
<td>L₁₉r-AlCu</td>
<td>-0.147</td>
<td>-0.139</td>
<td>-0.294</td>
</tr>
<tr>
<td>L₁₉r-AlZr</td>
<td>-0.469</td>
<td>-0.586</td>
<td>-0.429</td>
</tr>
<tr>
<td>L₁₉r-CuZr</td>
<td>-0.138</td>
<td>-0.038</td>
<td>-0.137</td>
</tr>
<tr>
<td>L₂₁-Cu₂ZrAl</td>
<td>0.117</td>
<td>-0.012</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4: Median error in mixing enthalpy, bulk modulus, and lattice parameter in reference to *ab initio* data for Cu-Zr-Al potentials with alloy components fitted in this work, developed by Sheng\(^5\)\(^2\)\(^6\), and potentials created using the Johnson alloy model\(^2\)\(^7\). The intermetallics used in testing include all 18 possible B1, B2, L1\(_0\), L1\(_2\), and L2\(_1\) compounds.

Our method was found to be comparable to the Sheng potential and far superior to the Johnson alloy model in replicating the mixing enthalpy and bulk moduli. When taking all 18 of the tested intermetallics into account, our method shows a median error of 0.057 eV in mixing enthalpy which is comparable to 0.077 eV obtained by using Sheng et al. potential and far below the median error of 0.385 eV of the potentials created by Zhou. Additionally, our method gives a median error of 2.9 GPa for bulk modulus of the tested intermetallics, which is significant improvement over the median error of 13.5 GPa and 16.8 GPa obtained by Sheng potential and Johnson alloy model potential,
respectively. The lattice parameters predicted by all three potentials are comparably accurate with the median error being less than 2% using all potentials. It is worth noting that the Sheng potential was found to have the least maximum error, with a maximum error of 5.7% for the $a$-direction lattice parameter of L1$_0$ AlZr. In comparison, the potentials created in this work and with the Johnson alloy model have a maximum error in this lattice parameter of 14.6% and 15.0%, respectively. So, it is evident that creating a sophisticated potential with a large training set will diminish the chances of having outliers by ensuring more compounds and bonding environments are sampled and fitted against. However, taking all intermetallics into account, our potentials demonstrate predictive capability comparable to a more sophisticated and computationally expensive potential and far superior to potentials developed using the Johnson alloy model.

Effectiveness in Simulating Metallic Glasses

In recent years, molecular dynamics has seen increasing use for the simulation of metallic glasses. In fact, many potentials are specifically tuned to accurately replicate the properties of liquids and amorphous alloys$^{54,55}$. In order to validate our method in reference to this application, a model of a Cu$_{45}$Zr$_{45}$Al$_{10}$ metallic glass was generated with each of the candidate potentials.

Each model was generated starting from the same randomly-seeded BCC lattice. The lattice was thermalized at 300 K, and then rapidly heated to 2000 K at $2.83 \times 10^{13}$ K/s. The system was equilibrated for 60 ps at that temperature and then quenched to 1500 K at $6.67 \times 10^{11}$ K/s. The model was then cooled to 200 K at an average rate of $1.0 \times 10^{11}$ K/s in temperature steps of 32.5 K. Starting at 1272.5 K, the quench rate was slowed by 12%
until 622.5 K, which is well below the calculated glass transition temperature near 740 K. After this point, the quench rate was returned to the pre-1272.5 K value. This non-linear quench schedule allows for minimal simulation time to be spent where there is either quick structural relaxation or frozen dynamics, while a slow quench rate is used around the glass-transition temperature, where it is crucial. The final structure at 200 K was then relaxed to 0 K using a conjugate-gradient minimization technique. The elastic constants of the 0 K structure were determined from the stress resulting from strains ranging from -0.8% to 0.8% in steps of 0.4% along all three axes.

**Figure 5:** Radial distribution functions of Cu_{45}Zr_{45}Al_{10} metallic glasses at 0 K produced using interatomic potentials developed in this work, by Sheng [50], and Zhou using the Johnson alloy model.
As a first test, the 0 K structure predicted by each potential was studied to determine if it was amorphous and to determine if any anomalous behavior occurred. All three potentials produced an amorphous structure, as evidenced by the non-zero minimum between the first and second peaks of the radial distribution function in Figure 5.

**Figure 6:** Aluminum distribution in Cu$_{45}$Zr$_{45}$Al$_{10}$ metallic glass at 0 K in 16000-atom models generated by simulating a rapid quench from the liquid state using potentials made by (a) this work, (b) Sheng$^{52}$, and (c) the Johnson alloy model$^{27}$. Sheng’s and our potentials show a uniform distribution of aluminum. In contrast, the Johnson alloy potential predicts a distinct demixing the aluminum, which is not likely for this alloy composition$^{57}$.

However, as shown in Figure 6, the Johnson alloy model predicts demixing of aluminum, which was found to occur immediately after melting. Even if demixing of the liquid was to occur at high temperature, such rapid and complete separation (which occurred in less than 20 ps at 2000 K) is unrealistic, especially considering that this composition is known for forming metallic glasses$^{57}$. This anomaly is most likely attributable to the large discrepancies in the predicted mixing enthalpies from the Johnson alloy model. While this does not prove that the potentials developed using the Johnson alloy model are ineffective in modeling glasses in general, it does show it to be ineffective in modeling the Cu-Zr-Al ternary and suggests that its reliability may be limited overall.
Table 3: Elastic and physical properties of a Cu_{45}Zr_{45}Al_{10} metallic glass predicted using molecular dynamics in comparison to experimental data\(^5\). The potentials include one generated in this work, a potential holistically fitted to alloy properties and the force-matching approach\(^5\), and a potential developed within the Johnson alloy model\(^2\). 

<table>
<thead>
<tr>
<th></th>
<th>Elastic Moduli [GPa]</th>
<th>Density at 300 K [g/cc]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Elastic</td>
<td>Shear</td>
</tr>
<tr>
<td>Sheng(^2)</td>
<td>72.0</td>
<td>25.8</td>
</tr>
<tr>
<td>Zhou(^2)</td>
<td>64.4</td>
<td>23.1</td>
</tr>
<tr>
<td>This Work</td>
<td>66.2</td>
<td>23.7</td>
</tr>
<tr>
<td>Experiment(^5)</td>
<td>99.1</td>
<td>36.3</td>
</tr>
</tbody>
</table>

The second test was to compare the elastic moduli and density predicted for the metallic glass with experimental values, as shown in Table 3. In terms of density, the potential developed by Zhou replicates the experimental value most accurately with only a 0.8% difference even though the predicted demixed structure is unrealistic. In contrast, the other two potentials predict densities between 4% and 5% lower than experiment, which is more plausible than the Johnson potential given that the density of an amorphous phase decreases with increasing quench rate. Additionally, the elastic moduli predicted by each potential are lower than experimental values, which can also be attributed to the extreme quench rate\(^5\). Even though there is a difference of 10% between the predicted elastic moduli of the different potentials, the fact that there is no experimental data from metallic glasses quenched at such high rates makes it imprudent to discredit any potential on the basis of the predicted properties. The relative agreement of our potential with the Sheng potential demonstrates that our method can be used to generate models of metallic glasses that replicate properties just as well as those created by more sophisticated techniques. And, given the lack of anomalous demixing, we also
assert that our method for generating alloy potentials is superior to mixing rules when modeling metallic glasses.

Advantages and Limitations of the Method

One of the main limitations of this method is the small training set used to develop the binary potentials. More thorough studies, such as Sheng’s potentials developed in\textsuperscript{52}, use a greater number of intermetallic compounds and other structures in their training sets. The broader range of atomic configurations evaluated by the fitting program directly corresponds to a denser set of pair distances and electron density values used in fitting the pair and many-body components of the EAM potential. Our method, in its current form, is not intended to generate “best-in-class” potentials but instead to enable the rapid evaluation of the alloy systems by reducing the size of the training set. However, we have found that the quality of our potentials for the test cases is very high – significantly better than the Johnson alloy potentials and very comparable to the “best-in-class” potentials.

The small number of \textit{ab initio} calculations required for a single binary system can be comfortably performed on a multi-core workstation, and are trivial on even a modest high-performance computer. Using that data to generate a binary potential only requires a few hours on a workstation and combining the binaries completes in seconds.

In addition to the reduced training set, our method is also limited by a dependence on the original potentials. This includes varying degrees of compatibility between elemental potentials developed by different authors, which has been addressed by using standardization transformations. Additionally, our potentials are limited by any inaccuracies present in the elemental potentials. This problem is present in any alloy
potential that did not have all components fitted simultaneously, and simply requires the
selection of elemental potentials suitable to replicate properties of interest in pure
systems.

One key goal of this work was to make the developed alloy potential database and
the computational tools freely available and easily accessible. A dedicated website has
been developed for this purpose\(^{59}\). The software tools used in this study are provided to
allow performing fits with different elemental potentials or a more-intensive fitting if
required for a specific problem. All components used in creating the fitting tool are
written in languages with free compilers or interpreters (Python, C/C++, and Octave) and
utilize LAMMPS, an open-source molecular dynamics package\(^{60,61}\). The \textit{ab initio}
calculations were performed with VASP\(^{62}\), though open-source options do exist\(^{63}\).

Conclusions

In this work, we present a method for rapidly creating alloy potentials with minimal
computational costs. The alloy potentials are created by using the pure-element
interaction terms from previously developed potentials and fitting the binary interactions
in the Finnis-Sinclair formulation of the EAM to \textit{ab initio} data. These binary potentials
can be combined to form multi-component potentials that maintain the accuracy of the
original elemental and binary systems with no additional fitting. Potentials created using
our method were demonstrated to be superior to alloy potentials generated using the
Johnson alloy model and comparable in accuracy to potentials that fit all interaction
terms simultaneously against a larger training set.
Chapter 3: Predicting Glass-Forming Ability

Introduction

Under typical circumstances, a metal alloy rapidly and spontaneously transforms from an amorphous liquid into a crystalline solid as cooled below the liquidus temperature. With careful selection of alloy composition and processing, it is possible to form metals into a glassy state. These metallic glasses possess unique properties, such as exceptional yield strength and soft magnetic behavior, which make them superior to conventional metal alloys for many applications\(^1\). However, the far-from-equilibrium structure that gives metallic glasses their extreme properties limits the thickness of cast parts and the composition of possible alloys. While the first metallic glasses could only be formed in thicknesses less than 100 \(\mu\)m, later alloys were discovered that could be cast in thicknesses well over 1 cm\(^6\). Since the advent of these “bulk metallic glasses” (BMGs), finding new BMGs and studying what allows them to so easily avoid crystallizing has been a central issue in the field\(^1,5\).

To date, the standard method for identifying glass forming alloys has been based on a series of empirical rules\(^5\). For instance, it is generally accepted that incorporating many alloying elements of different sizes “frustrates” crystallization. This concept is based on
the idea that the inclusion of different atomic radius ratios can lead to the formation of metastable, but amorphous structures in the glasses. Another common rule for selecting the optimum balance of these alloying elements is to use compositions near deep eutectics, where the liquid phase is particularly stable. However, it is often difficult to locate these eutectic compositions in multi-component alloys. Many studies have been successful in discovering BMGs using experimental trial-and-error searches through a materials system guided by these rules, but such an approach can be slow and costly.

To offset this limitation of experimental work, a number of previous studies have sought to predict candidate regions for glass formation using computational methods. The proposed methods use tools ranging from molecular dynamics to computational thermodynamics to predict whether alloys will have characteristics required for glass formation, such as low driving force for crystallization, slow dynamics, and energetic stability. To our knowledge, no method proposed to date has been able to accurately predict compositions with high glass forming ability without any experimental input. At best, it has been possible to utilize large experimental databases and computational thermodynamics to locate alloys in select systems.

In this work, we integrate the most promising strategies for predicting glass-forming ability into a single computational tool that utilizes classical molecular dynamics. The empirical potentials used in classical molecular dynamics are available for a large number of systems, and can be generated using ab initio data. It is therefore possible to evaluate a new alloy system without the need to cast any glass or gather a thermodynamic database.
**Background**

We propose to identify potential BMGs by identifying regions of high glass forming ability based on a figure of merit combining kinetic and energetic considerations. The first factor in our model, the liquid fragility, describes the kinetics of the liquid. It is a measure of how the viscosity changes with temperature close to the glass transition, $T_g$. Liquids with a low fragility index, $m$ (Eq. (16)), have a high viscosity, $\eta$, (and therefore limited atomic mobility) in the supercooled liquid, which stifles crystal growth. This parameter has been correlated with glass forming ability, and previously used in search for metallic glasses in the Ca-Mg-Zn system based on experimental values. Fragility was also chosen because it is easily accessible to classical molecular dynamics calculations.

As a second factor, we propose characterizing the relative energetic driving force for crystallization in the glasses using the concentration of stable atomic clusters. In the 1950s, F.C. Frank hypothesized that efficiently-packed atoms arranged in clusters that lack symmetry suitable for crystal formation lead to the stability of supercooled liquids. His original work proposed that icosahedral clusters fit that criteria for monotonic systems and should be prevalent in supercooled metals. These clusters have been also found in supercooled liquids of amorphous alloys and tied to nucleation barrier for glass formation in multi-component systems. Additionally, Miracle et al. have developed a method to identify efficiently-packed clusters based on the composition of the cluster and the atomic radii of the constituents, which have been tied to the composition of eutectics and glass forming alloys.
Methods

Model Generation

Periodic cells of 11,664 and 16,000 atoms were used for the binary and ternary systems, respectively. To create a model of a metallic glass, a body-centered cubic lattice was initially randomly seeded with atoms to achieve the desired composition. The system was then thermalized at a temperature of 300 K and heated to 3000 K at $6.75 \times 10^{13}$ K/s. After 40 ps of equilibration at 3000 K, the system was cooled to 1500 K at $7.5 \times 10^{11}$ K/s. The model was then quenched to 200 K at a nominal rate of $1.0 \times 10^{11}$ K/s in temperature steps of 32.5 K. Between 1272.5 K and 622.5 K (around the simulated glass transition temperatures of 710-800 K), the number of timesteps at each subsequent temperature step was increased by 12% to allocate additional simulation time where the dynamics are slowest. Below 622.5 K, the number of timesteps was decreased to the pre-1272.5 K value in consideration of the abrupt decrease in the atomic mobility after the glass transition.

Fragility Calculation

At temperatures ranging from 750 K – 1150 K, the viscosity $\eta$ of each model was determined using a Green-Kubo relation\textsuperscript{73,74} in the form

$$\eta = \frac{V}{k_B T} \int \langle P^{\alpha\beta}(t) P^{\alpha\beta}(t_0 + s) \rangle ds,$$  \hspace{1cm} (15)

where $V$ is the volume of the simulation cell and $P^{\alpha\beta}$ is a shear component of the stress tensor. The autocorrelation function was averaged using 30,000 distinct time origins, and the integral was taken over 0.1-10 ns (varying with temperature). To improve
the accuracy of the calculated fragility, the average over all three independent, off-diagonal elements of the stress tensor was used in calculating the autocorrelation function\textsuperscript{75}. The Vogel-Fulcher-Tammann (VFT) relationship for the temperature dependence of viscosity was then fitted to the calculated viscosities, as it is known to describe metallic glasses well experimentally\textsuperscript{76}. The fragility ($m$) was then determined as

$$m = \frac{d \log(\eta)}{d(T_g)} \bigg|_{T=T_g},$$

(16)

where $T_g$ is defined as the temperature at which $\eta = 10$ Pa-s. This viscosity was chosen because it is the average viscosity at the glass transition temperature determined by the variation in volume with temperature for all tested binary systems.

The fragility calculation was repeated for 15 different quench iterations for each composition. The resultant properties were combined into an average weighted by Boltzmann factors according to the system energies at 800 K.

\textit{Structural Analysis}

The models of the metallic glass at 300 K achieved near the end of the cooling simulations were structurally relaxed by driving them to the closest local energy minimum using a conjugate-gradient algorithm. These low-temperature structures were studied as an approximation for the structure just above the glass transition temperature, as significant structural rearrangement will have ceased in the glassy state.

First, the geometric nearest neighbors for each atoms were identified using a radical Voronoi tessellation method\textsuperscript{77} with atomic radii determined from the partial radial distribution functions of Cu\textsubscript{50}Zr\textsubscript{50} (1.28 and 1.60 Å). Neighbors that correspond to faces
less than 1% of a Voronoi cell surface area are removed to compensate for the effect of
fluctuations in atomic position and numerical issues intrinsic to Voronoi tessellations\textsuperscript{78}.

The icosahedral clusters in the model were then identified as atoms coordinated with
dozen neighbors that are each coordinated with exactly five other atoms in that neighbor
shell. Efficient clusters using the effective radius ratio method were also identified based
on the type of atoms in each atom’s coordination shell. Using the methods described in\textsuperscript{71},
the fraction of clusters with an Atomic Packing Efficiency (APE) parameter of less than
\pm1\% was determined. The APE is defined such that zero corresponds to the effective
radius ratio of the neighbors to the central atom being equal to the ideal ratio for a cluster
with that number of atoms.

As with fragility, the fraction of efficient and icosahedral clusters was calculated for
all 15 quench iterations for each composition and averaged using a Boltzmann-weighted
average at 800 K.

Results and Discussion

\textit{Development of Figure of Merit}

As shown in Figure 7, the fragility calculated using molecular dynamics captures the
regions of low fragility in the Cu-Zr binary system found in experiment, with minima
near Cu\textsubscript{65}Zr\textsubscript{35} and Cu\textsubscript{45}Zr\textsubscript{55}. In contrast, the population of icosahedral and efficiently
packed clusters, which are both considered to help stabilize the supercooled liquid against
crystalization, both increase with Cu fraction in the Cu-Zr binary, as shown in Figure 8.
This is surprising since these two clusters are not equivalent; icosahedral clusters are
neither always efficiently packed nor the only type of efficient cluster based on the
effective radius ratio method. In the Cu-Zr binary, we found there are always more efficient clusters than icosahedral clusters, and the concentration of efficient clusters increases at a faster rate with Cu fraction. Based on the differences in description and behavior in the tested binary, we conclude that each cluster type must be considered independently when assessing glass-forming ability.

Figure 7: Fragility in the Cu-Zr binary system calculated from molecular dynamics simulations (this work) and experimentally measured\textsuperscript{79}. The two data sets are normalized such that the fragility of Cu\textsubscript{56}Zr\textsubscript{44} is equal to unity to account for the quench rate dependence of the fragility\textsuperscript{80}. Error bars represent the standard error of the mean.

In order to assign an effective weight to the fragility and stabilizing clusters, the variation of each factor was studied with reference to glass forming ability in the Cu-Zr binary system. In this system, BMGs (here defined as: able to be cast in fully glassy rods more than 1 mm in diameter) have been reported for several compositions in the tested
range (Cu$_{65}$Zr$_{35}$ to Cu$_{40}$Zr$_{60}$) [81]. The icosahedral and efficient cluster fractions, however, strongly increase with copper concentration, as shown in Figure 8. If one considers any combination of these cluster fractions alone, it would suggest that BMGs would only be found in high-Cu regions, which is in disagreement with experiment. This implies that glass-forming ability does not correspond to the concentration of these favorable clusters alone and that some other factor must be taken into consideration.

![Graph showing concentration of icosahedral and efficient clusters](image)

**Figure 8:** Fraction of all atoms that are the center of an icosahedral cluster or the center of a efficient cluster identified using the Effective Radius Ratio method for the Cu-Zr binary system [71]. Compositions with a higher fraction of these clusters should demonstrate increased stability in the supercooled liquid. Error bars represent the standard error of the mean, and are smaller than the symbols.

Fragility, on the other hand, shows two local minima at a high and lower Cu concentration, as shown in Figure 7. While there is qualitative agreement, fragility alone
does not correlate perfectly with glass forming ability, which is well known experimentally\textsuperscript{10,67,82}. This is evident in our computational study, as Cu\textsubscript{40}Zr\textsubscript{60} has a lower fragility than Cu\textsubscript{50}Zr\textsubscript{50} but is known experimentally to have a smaller critical casting thickness. This shows clearly that fragility alone is also insufficient for use as a predictive tool and should be coupled with some other parameter, although it seems to be a better indicator than cluster fractions. Similar conclusions have been found within a more experiment-based approach, where the experimentally-determined fragility combined with crystallization driving force calculated through computational thermodynamics has been shown to correlate well with critical casting thickness\textsuperscript{10}.

We propose using a simple approach to combine the kinetics and energetic driving force information to form a figure of merit $K$,

$$K = \frac{I + E}{m^\alpha}$$  \hspace{1cm} (17)

In this form, $m$ represents the fragility, $I$ the fraction of icosahedrally-coordinated atoms, $E$ is the fraction of efficiently-packed clusters, and $\alpha$ is a weight factor designed to vary the relative contribution of kinetics and the energetic driving force. We combine the icosahedral and efficiently packed cluster fractions into a single term as they are both hypothesized to contribute to the energetic stability of the liquid. Fragility, on the other hand, is reasoned to describe the speed of atomic rearrangement in the liquid and was therefore treated as a distinct factor. These two factors do not appear to be correlated, further supporting treating them as independent terms in a figure of merit. While the chosen functional form of the figure of merit in Eq. (17) should be reasonable, we point out that it is not the only possible choice and presently has not been optimized. However,
we show below that the chosen expression has good predictive power, thus giving support to the chosen formula.

As fragility was found to have a stronger correlation with glass forming ability, a strong weight should be applied to the calculated fragility in our figure of merit. However, the relative contribution of each of these factors may vary between systems, so the appropriate magnitude of the factor may vary. For the Cu-Zr binary, as discussed in the next section, a weight factor ($\alpha$) of 6 was adopted in order to reach reasonable agreement with experimental observation. However, it was found that the same three regions are identified for improved glass forming ability as long as the weight factor was between 4 and 9. This range is consistent with the idea that fragility alone is insufficient to describe glass-forming ability and, therefore, should not be the only or completely dominant factor. On the other end, its importance is more strongly related to glass-forming ability than simply the efficient cluster fractions, which can be viewed in this formulation as a corrective factor. As long as fragility is a better predictor of glass-forming ability, this method can still be used in a predictive manner in any system. The relative insensitivity of our predicted regions to changes in the weight factor implies that it should be possible to use our figure of merit to identify favorable glass forming regions in other alloy systems as well, but not necessarily capture the relative magnitudes of critical casting thickness in each region.

*Accuracy in the Cu-Zr Binary System*

Validating our model is complicated by the fact that there is significant variation in glass forming ability reported from different casting methods and within the same casting
method. As an example, Figure 9 shows the predicted glass forming ability parameter in comparison to experimental critical casting dimensions in the Cu-Zr system, obtained from wedge castings (Figure 9a) and rods (Figure 9b). Having different experimental studies report different absolute dimensions is not surprising, given the large effect of various casting conditions (e.g. melt temperature, drop distance to the mold) on the effective cooling rate\(^8^3\). However, disagreement between the two casting geometries in whether a composition is reported as a local maximum in glass forming ability is a major concern. For instance, Cu\(_{56}\)Zr\(_{44}\) is reported as a maximum in two wedge casting studies\(^8^4,8^5\), but has never been identified as a maximum in a rod casting experiment. And, to further add to the confusion in the literature, Cu\(_{56}\)Zr\(_{44}\) was found to have a critical cooling rate five times faster than Cu\(_{62}\)Zr\(_{38}\) via quenching induced by gas atomization\(^8^6\), which is not supported in wedge-casting experiments. The different experimental methods are also in disagreement at Cu\(_{46}\)Zr\(_{54}\). This alloy is reported to have minimal glass forming ability via two wedge casting studies, but can be formed into plates with superior thickness\(^8^7\).
Figure 9: Figure of merit for glass forming ability in Cu-Zr binary system, calculated from the predicted fragility and stable cluster fractions, plotted in comparison with experimentally measured critical casting thicknesses\textsuperscript{84,85,87–94}. The predicted glass forming ability is shown in comparison to (a) wedge and (b) rod casting thicknesses separately. The three peaks in our computational figure of merit near Cu\textsubscript{62}Zr\textsubscript{38}, Cu\textsubscript{50}Zr\textsubscript{50}, and Cu\textsubscript{46}Zr\textsubscript{54} correspond to the three alloys with the highest rod critical casting diameter. The red (dashed) line averages the experimental data points to guide the eye.
Our proposed method identifies peaks in glass forming ability at Cu$_{62}$Zr$_{38}$, Cu$_{50}$Zr$_{50}$, and Cu$_{46}$Zr$_{54}$. If one considers only the local maxima of the system and disregards the actual magnitudes of the reported casting thicknesses due to the experimental disagreement, experiment suggests that there are four favorable alloy compositions in the binary system: Cu$_{64}$Zr$_{36}$, Cu$_{56}$Zr$_{44}$, Cu$_{50}$Zr$_{50}$, and Cu$_{46}$Zr$_{54}$. Our method is successful in identifying peaks in glass forming ability near all of those compositions with the exception of Cu$_{56}$Zr$_{44}$. It is unclear in the available literature whether it is possible to form fully amorphous specimens of Cu$_{56}$Zr$_{44}$ with a thickness comparable to that of the other three alloy compositions, as the partially crystalline, wedge casting results disagree with two other experimental techniques and our computational method. Regardless of whether that composition is a valid maximum in glass forming ability, our method does identify the three maxima shown by fully-amorphous casting experiments and shows promise in being able to identify suitable regions for further experimental study without need for experimental input.

Our method is a significant improvement over current empirical rules for locating metallic glass alloys. For example, the eutectic compositions in the Cu-Zr system near 38, 44, and 54 at% Zr do correspond to glass compositions with high critical casting thicknesses. However, searching only eutectics would fail to identify Cu$_{50}$Zr$_{50}$ as a top glass forming composition. At this composition, a liquid undergoes a congruent transformation and not a eutectic reaction during equilibrium solidification. The existence of glasses on non-eutectic compositions coupled with the difficulty in finding eutectics in multi-component systems experimentally makes our computational method clearly
advantageous in isolating glass forming regions in comparison to empirical rules in the Cu-Zr binary system.

**Application to the Cu-Zr-Ti Ternary System**

In order to further evaluate the proposed method, we chose to study two lines of constant copper concentration in the Cu-Zr-Ti ternary system, Cu\textsubscript{50}Zr\textsubscript{50-x}Ti\textsubscript{x} and Cu\textsubscript{60}Zr\textsubscript{40-x}Ti\textsubscript{x}. To even further test the versatility of the system, we chose to use potentials that were not specifically developed to model liquids, unlike those used in the Cu-Zr binary test described above\textsuperscript{54}. These potentials are part of a database originally developed to model crystalline structures and are not even specifically fit to model the Cu-Zr-Ti ternary system\textsuperscript{27}. In this case, the cross-interactions between different atomic species were described using the Johnson alloy model, a fast but rather approximate method\textsuperscript{31}.

Figure 10 shows the variation in glass forming ability as a function of titanium fraction for each alloy series, calculated using Equation 17 with α set to 6. For the 50 at% Cu series, our calculation method identifies Cu\textsubscript{50}Zr\textsubscript{42.5}Ti\textsubscript{7.5} as the best glass former, which is consistent with experimental observation\textsuperscript{95}. The method was also effective in finding a local maximum at Cu\textsubscript{50}Zr\textsubscript{15}Ti\textsubscript{35}, which is within 5 at% of the experimentally identified optimal composition at Cu\textsubscript{50}Zr\textsubscript{10}Ti\textsubscript{40}. Furthermore, we were able to predict that Cu\textsubscript{60}Zr\textsubscript{30}Ti\textsubscript{10} is the optimal composition in the Cu\textsubscript{60}Zr\textsubscript{(40-x)}Ti\textsubscript{x} system, which is consistent with experiment\textsuperscript{96}. In short, this technique was generally successful in locating high glass forming ability compositions in the Cu-Zr-Ti system and shows that it can be used with general-use interatomic potentials. Therefore, this method seems to be forgiving with respect to the quality of the potentials used, which should be helpful when examining
multicomponent alloys for which potentials have to be created. The fast method to quickly develop alloy potentials described in Chapter 2 will allow more global searches for good glass formers in the future by being able to develop even better alloy potentials\textsuperscript{97}.

In contrast, empirical rules for locating glass forming compositions are less effective in Cu-Zr-Ti system. Neither of the alloy series directly sample a ternary eutectic composition\textsuperscript{98}. Of the two tested series, Cu\textsubscript{50}Zr\textsubscript{50-x}Ti\textsubscript{x} passes close to a eutectic at Cu\textsubscript{48.6}Zr\textsubscript{37.5}Ti\textsubscript{13.9}, but the optimal alloy composition is not the one with the greatest proximity to the eutectic\textsuperscript{95}. In the Cu\textsubscript{60}Zr\textsubscript{(40-x)}Ti\textsubscript{x} series, it would not be feasible to apply the eutectic search as no eutectic compositions are close to that composition line. This failure of empirical rules further illustrates their weakness and the relative advantage provided by a computational search before experimentation.
Figure 10: Figure of merit for glass forming ability in the (a) Cu$_{50}$Zr$_{(50-x)}$Ti$_x$ and (b) Cu$_{60}$Zr$_{(40-x)}$Ti$_x$ systems, calculated from the predicted fragility and stable cluster fractions. Cu$_{50}$Zr$_{42.5}$Ti$_{17.5}$ exhibits the clear maximum in glass forming ability in the Cu$_{50}$Zr$_{(50-x)}$Ti$_x$ system, which is also observed experimentally$^{95}$. The highest predicted glass forming ability in the Cu$_{60}$Zr$_{(40-x)}$Ti$_x$ system is found for Cu$_{60}$Zr$_{30}$Ti$_{10}$ in agreement with experiment as shown by the vertical dashed line in (b)$^{95}$. 

47
**Advantages of Method**

Our proposed method shows promise in being able to locate optimal alloy compositions in the Cu-Zr-Ti ternary system and can be easily applied to other systems. Molecular dynamics is not limited by any number of components and only requires interatomic potentials, of which there are several databases\textsuperscript{25–27}. We have found that the potentials do not need to be specifically tuned to modeling liquids, so the “general purpose” potentials available in these databases should be suitable to a wide degree. The computational requirements for this work are significant, but are easily attainable on a high-performance cluster. Furthermore, the required software can be run on any system, and will be made available with appropriate documentation on http://atomisitcs.org.ohio-state.edu.

One current limitation of this method (and experimental studies) is that searching an entire ternary or higher-order system would require testing a large number of materials. To accelerate identification of glass forming alloys, a computationally faster method to “pre-screen” the system to locate potential glass forming regions would be a significant improvement. One potential method is to identify composition regions that are suitable for forming efficiently packed, amorphous structures. As shown above, the fraction of these clusters alone is insufficient to determine glass-forming ability. However, previous work has shown that metallic glasses tend to form near compositions that reflect the compositions of efficient clusters\textsuperscript{72}, suggesting they may be at least a requirement for glass formation. If this method is used to identify interesting regions and combined with the simulation methods from this work, one could create a method for rapidly and
accurately assessing many-component systems in a large space of elements and compositions for regions of high glass forming ability.

Conclusion

In summary, this work proposes a novel computational approach for prediction of glass forming ability in metallic glasses. By combining the calculated fragility with icosahedral and efficient cluster fractions based on molecular dynamics simulations, it is possible to identify the optimal glass forming compositions. These tools have been shown to be consistent with experimental observations in the Cu-Zr binary and Cu-Zr-Ti ternary system and can be easily used in other systems. This method alone, or in combination with other tools, can be used to enable the design of metallic glasses with limited and efficient experimentation.
Chapter 4: Automated Design of Metallic Glasses

Introduction

The benefits to having a computational way of designing materials are simple and well-known: a large number of time-, labor-, and resource-consuming experiments can be replaced by an automated computer program. In the past decade and especially in the past few years, there has been a large push in the materials engineering community towards strongly integrating the use of computational tools in the development of new materials visible in programs such as Integrated Computational Materials Engineering and the Materials Genome Initiative. There is already a limited number of success stories in using computational methods to design materials ranging from lithium-ion batteries\textsuperscript{99} to blast-resistant steels\textsuperscript{100}. And, concurrently, there has been a large advancement in computing power enabling high-throughput methods for rapidly assessing the properties of a large number of materials across a large composition space\textsuperscript{101–103}. 

For metallic glasses, one of the more promising techniques for computational design is a computer-based search through a large composition space guided by some sort of optimization algorithm. The possible composition ranges for metallic glasses are so diverse that an exhaustive search of compositions would be impractical, although an unguided search is useful in some material systems\textsuperscript{104}. The use of optimization algorithms is not a new idea in materials engineering and has been demonstrated in designing core-shell nanoparticles\textsuperscript{18} and ordered metallic alloys\textsuperscript{17}. These studies found
that using a global search algorithm, such as genetic algorithms, will drastically reduce the time required to locate an optimal candidate.

The goal of this work is to implement such a computational design scheme for metallic glasses. This system will require a database of interatomic potentials, which was developed in Chapter 2. And, when combined with the glass-forming ability prediction methods presented in Chapter 3, it will be possible to design metallic glasses with little to no experimental input.

Methods

In this work, we used two different studies to assess the effectiveness of our approach for designing a ternary metallic glass. The first study was used to assess the fundamental possibility of optimizing properties and integrating such a search with glass-forming ability calculations. The second test was designed to evaluate the effectiveness of genetic algorithms.

Optimization Strategy

For both tests, the compositions were bounded by an imposed maximum of 90 at% for the composition of any of the three constituents and were specified in discrete intervals of 0.2 at%. An elitist genetic algorithm was chosen to locate the optimal composition in this sample space because it does not require the fitness function to be differentiable and is able to find a global extremum. The genetic algorithm works by creating a pool of candidate materials that includes a selected number of the best materials tested so far. Individuals are randomly selected for crossover with probabilities equivalent to their relative fitness. The crossover between two individuals is
accomplished by randomly selecting the constituent elements with equal probability. The compositions are either randomly selected from either parent or the average of the two parents is selected with a small probability. During the mutation phase, the constituent elements or the composition can be randomly changed. The probability of mutation decays from 70% to 30% by 1% after each new individual is made. After the crossover and mutation, the composition is adjusted so that it adds to 100 at% and no constituent is repeated.

In the first test, our goal was to locate an alloy with high stiffness-to-density ratio using Ni, Cu, Zr, and Ti as possible constituents using the figure of merit

\[ F = \left( \frac{E}{\rho} (1 - x)^8 \right)^3, \tag{18} \]

where \( E \) is the elastic modulus, \( \rho \) is the density, and \( x \) is the fraction of the atoms in a crystalline structure. The crystal fraction term was included in order to apply a penalty to materials that crystallized under computational conditions. This figure of merit was cubed for use as a weighting factor in order to exaggerate small differences. This test was run before the alloy potentials described in Chapter 2 were completed and thus with the potentials developed by Zhou using mixing rules for alloy components \(^{27}\), with the knowledge that they can be unreliable but still produce decent property estimates in metallic glasses (see Chapter 2). The selection pool contained 6 top alloys and 4 other alloys that were generated most recently. The first 15 materials generated by the algorithm were selected randomly and followed by 65 generated using the genetic algorithm. The minimum mutation probability was set to 35%.
The goal of the second study was to determine a metallic glass with the highest elastic modulus using the constituents Ni, Nb, Al, Zr, Ti, and Ta. The possible composition space for this problem with the discretization chosen includes over 1 million possible alloys, which is approximately five times larger than the field from the first test. The figure of merit ($F$) used in this study was

$$F = [E(1 - x)^8]^2,$$  \hfill (19)

where $E$ is the elastic modulus and $x$ is the fraction of the atoms in a crystalline structure. The square of this figure of merit was used as a weight factor when materials were randomly selected for optimization purposes. The selection pool for this test contained 20 materials, 15 of which were the best tested so far. The optimization algorithm sampled 30 random compositions before generating 90 via the genetic algorithm.

**Automation Software**

A software program was developed in order to completely automate the composition optimization. This program keeps track of the components and properties of the tested materials, manages the calculations, and centralizes the data retrieval. The program is written in a commonly-used language (C++) and designed in such a way to allow for easy adaptation to new problems and optimization techniques. The source code is available at http://atomistics.org.ohio-state.edu/.

**Model Generation**

Models of metallic glasses were generated using classical molecular dynamics with embedded-atom method potentials developed using the techniques described in Chapter 2. To create a model of the amorphous metal, a BCC lattice of 16,000 atoms was
first randomly seeded with atoms at the desired composition. This model was then thermalized at 300 K and heated to 3000 K at a rate of $6.75 \times 10^{13}$ K/s. After 600 ps of equilibration, the model was cooled at $3.75 \times 10^{11}$ K/s to 2100 K and then at $6.75 \times 10^{13}$ K/s to 200 K. The model of the metallic glass at 200 K was then quenched to the 0 K structure using a conjugate-gradient algorithm.

**Property Calculation**

The fraction of atoms in a crystalline region was determined by using a radical Voronoi tessellation to determine the neighboring atoms for each atom in the simulation cell\(^{105}\). Any face of the Voronoi cell of each atom that is smaller than 1\% of the surface area of the cell was removed to compensate for the tendency of Voronoi tessellations to overestimate the number of neighbors for each atom\(^ {78} \). Each atom was assigned a cluster shape of the form: $<n_3,n_4,n_5,n_6>$, where $n_i$ corresponds to the number of neighboring atoms bonded to $i$ other atoms in the cluster with the center atom not counted\(^ {106} \). Atoms are counted as part of a crystalline cluster if they have an index of $<0,12,0,0>$ or $<0,6,0,8>$, which are consistent with FCC/HCP and BCC crystal structures, respectively.

Given the rapid quench rate, more-complex crystal structures and intermetallics are not expected to form on cooling.

The elastic properties of the glass were determined by applying small strains to the metallic glass at 0 K and relaxing the atom positions using the FIRE method\(^ {107} \). Strains ranging from -0.8\% to 0.8\% in steps of 0.4\% are applied in the x, y, and z directions, for a total of 125 test points. The elastic constants of this material were determined from the $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$ of the model at each strain level. Using the assumption that the glass is
isotropic, this only requires fitting two elastic constants (C\textsubscript{11} and C\textsubscript{12}). We found that the stress-strain behavior of our glasses is described under this assumption.

Results and Discussion

Test #1: Integration with Glass-Forming Ability

The top four alloys from our first test of the optimization program system are shown in Table 4. These alloys have small crystal fractions, so the figure of merit (Eq. 18) is roughly equivalent to the elastic modulus to density ratio of the glass. Based on this result, we tentatively propose that a Ti\textsubscript{60}Ni\textsubscript{40} metallic glass base would have the optimal stiffness-to-density ratio for any metallic glasses in the Ni-Cu-Zr-Ti system with up to three components. Additionally, as demonstrated by the 3\textsuperscript{rd} best material, Ni\textsubscript{60}Ti\textsubscript{40} is also a promising candidate. The minor additions to both of these alloys should be important but, for simplicity, are ignored at this stage.

Table 4: Ni-Cu-Zr-Ti based metallic glasses that were tested by the materials design program with the best stiffness-to-density ratio.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Figure of Merit [GPa-cm\textsuperscript{3}/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti\textsubscript{61.0}Ni\textsubscript{38.0}Cu\textsubscript{0.4}</td>
<td>13.00</td>
</tr>
<tr>
<td>Ti\textsubscript{61.2}Ni\textsubscript{38.8}Zr\textsubscript{0.8}</td>
<td>12.99</td>
</tr>
<tr>
<td>Ni\textsubscript{62.0}Ti\textsubscript{37.6}Cu\textsubscript{0.4}</td>
<td>12.96</td>
</tr>
<tr>
<td>Ti\textsubscript{61.2}Ni\textsubscript{38.4}Cu\textsubscript{0.4}</td>
<td>12.95</td>
</tr>
</tbody>
</table>
**Figure 11:** Glass-forming ability of Ti$_{100-x}$Ni$_x$ binary metallic glasses calculated using a molecular-dynamics method.

In order to assess the feasibility of integrating this property optimization method with our computational assessment of glass-forming ability, we located the optimal alloy for glass-forming ability near the optimal property result of Ni$_{40}$Ti$_{60}$. Using the methods described in Chapter 3, we calculated the fragility of the supercooled liquid and the fraction of icosahedral and efficiently-packed clusters for several compositions in the Ni-Ti binary. These calculations were performed with an interatomic potential developed using our alloy potential creation method in order to ensure better property prediction than with the potentials initially used in property optimization. The glass-forming ability of each of these compositions was calculated using Equation 17 from Chapter 3.
where $I$ is the fraction of icosahedrally coordinated atoms, $E$ is the fraction of atoms that are the center of an efficiently-packed cluster, and $m$ is the fragility of the liquid. The weight factor ($\alpha$) was set to 6, the same value used for calculations in the Cu-Zr-Ti ternary. As shown in Figure 11, the best composition for glass-forming ability was found to be Ti$_{70}$Ni$_{30}$. This composition is experimentally known to be able to be formed into an amorphous ribbon using melt spinning\textsuperscript{108}. And, based on elastic property and density measurements with the new potential, this alloy should also have a similar stiffness-to-density as the originally proposed alloy, Ti$_{60}$Ni$_{40}$.

**Test #2: Algorithm Effectiveness**

As a result of the larger composition space, the results from the second test were used to assess the algorithm effectiveness. Figure 12 shows the figure of merit (Equation 19) for each material tested during the optimization run in the order they were created. The first 30 materials were randomly generated and the remaining 90 were generated iteratively using a genetic algorithm. As shown by the black dashed line, materials with progressively higher figures of merit were gradually located as more were tested. And, shown by the red solid line, the average figure of merit increased as more better-performing materials were located and included in determining the next guesses.
Figure 12: Figure of merit of materials tested in the optimization run in the order they were created. The dashed line indicates the maximum of the materials tested so far. The solid line is the average of the last 10 materials that were tested.

While we did not test any other optimization algorithms, we did find the genetic algorithm locates better materials than random searching. The average figure of merit of the 30 materials generated randomly was approximately 98.9 GPa. In comparison, the average figure of merit of the last 30 materials created using the genetic algorithm was 188 GPa. This increase in the average fitness shows that the genetic algorithm is effective in accelerating the search for optimal materials. In systems with even more potential constituents and possible combinations, an optimization algorithm will be even more necessary to sort through all of the possible combinations. During the random search
stage of our optimization a material with a figure of merit within 10% of the optimal material was found, but this fortunate occurrence becomes more unlikely with larger numbers of combinations. While the genetic algorithm used in our study was successful in accelerating our search, we do not have any evidence that it is the optimal search technique. For example, it could be possible to further accelerate this search using a simplex algorithm\textsuperscript{109} or a combination of simplex and genetic algorithms\textsuperscript{22}.

\textit{Test #2: Alloy Prediction}

The top alloys identified by our design program for the second test along with their figure of merit are shown in Table 5. All of the top six of the 120 tested alloys are in the Ni-Nb-Al system. As all have crystal fractions that are much less than 0.1%, and thus the figure of merit (shown in Equation 19) is approximately equal to the elastic moduli of these materials.

\textbf{Table 5:} Materials that were tested by the materials design program with the best figure of merit.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Elastic Modulus [GPa]</th>
<th>Figure of Merit [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\textit{Our Study}</td>
<td>\textit{Mixing Rule}</td>
</tr>
<tr>
<td>Ni\textsubscript{66.4}Nb\textsubscript{21.4}Al\textsubscript{12.2}</td>
<td>220.0</td>
<td>163.8</td>
</tr>
<tr>
<td>Ni\textsubscript{46.6}Nb\textsubscript{41.6}Al\textsubscript{11.8}</td>
<td>219.1</td>
<td>145.1</td>
</tr>
<tr>
<td>Ni\textsubscript{70.3}Nb\textsubscript{22.6}Al\textsubscript{6.6}</td>
<td>216.0</td>
<td>170.0</td>
</tr>
<tr>
<td>Nb\textsubscript{49.4}Ni\textsubscript{35.2}Al\textsubscript{15.4}</td>
<td>213.1</td>
<td>133.0</td>
</tr>
<tr>
<td>Nb\textsubscript{57.0}Al\textsubscript{15.4}Ni\textsubscript{17.6}</td>
<td>212.3</td>
<td>112.8</td>
</tr>
<tr>
<td>Nb\textsubscript{59.4}Al\textsubscript{25.6}Ni\textsubscript{15.0}</td>
<td>210.8</td>
<td>110.3</td>
</tr>
</tbody>
</table>

The alloys predicted using our method are much different than what would be expected using mixing rules, which are hypothesized to accurately predict the elastic moduli of metallic glasses\textsuperscript{110}. Of the materials that were tested by our optimization program, one would predict Ni-Ta alloys to have the highest elastic moduli, with elastic
moduli between 180 and 195 GPa. The alloys predicted using our method are not even in the top 10 tested alloys based on their mixing rule elastic moduli, and have moduli over 10% lower than the Ni-Ta alloys, as shown in Table 5. Based on mixing rules alone, the optimal metallic glass would be a pure Ni alloy with an elastic modulus of 200 GPa. This alloy will likely have minimal glass-forming ability, which highlights that mixing rules do not have any capability for taking any glass-forming ability into account. Without experimental validation, it is not currently possible to assess whether our molecular dynamics based method is accurate for predicting elastic moduli than mixing rules.

Computational Feasibility

This method does require significant computational resources. Building the model and calculating properties of a single composition requires approximately 12 days on a modern processor. Completing a run of 120 materials on a four processor workstation would take nearly a year. With the use of a modest computer cluster of less than 150 processors, the whole optimization run can take less than 3 weeks. While this is a significant computational requirement, it is easily achievable with access to a high-performance computer.

Conclusion

In this work, we demonstrated a technique for locating metallic glasses with optimal properties using a genetic algorithm and properties calculated using classical molecular dynamics. We identify a Ni\textsubscript{66.4}Nb\textsubscript{21.4}Al\textsubscript{12.2} as the approximate composition of a ternary metallic glass in the Ni-Nb-Al-Zr-Ti-Ta system with the highest elastic modulus, which would not be predicted using mixing rules. Additionally, we identified Ti\textsubscript{70}Ni\textsubscript{30} as the
metallic glasses with the maximum stiffness-to-density ratio in the Ni-Cu-Zr-Ti quaternary. Pending experimental evaluation, we propose this method as an effective tool for accelerating the search for metallic glasses with a desired balance of properties.
Future Work

Future work in creating interatomic potentials could focus on utilizing more efficient algorithms for fitting function parameters, which is currently the rate-limiting step of the process. Also, including the stiffness matrix or elastic modulus plus Poisson ratios of the fitted crystals into the training set could improve the quality of the property predication potentials. Finally, the software currently does not have the ability to apply transformations that would further increase the accuracy of alloy potentials, but would prevent them from being combined with other alloy components\textsuperscript{29}. This will allow for creating more accurate potentials for specific alloys. If this feature is implemented, the software should also be extended to support fitting potentials with more than two components.

The focus of the other two projects in the future will be validation of the predicted alloys. The glass-forming ability work has not yet been used to identify metallic glasses in a previously-unstudied composition region – a key step in assessing its capability and locating limitations. The glass-forming ability methods could also benefit from improvements to its speed. One possible change is using diffusivity instead of viscosity when measuring the temperature dependence of kinetics in the supercooled liquid. This calculation is much less time and disk space intensive, but does not have the backing of any precedence in the literature. Additionally, the property design software could benefit from optimization of the genetic algorithm parameters.
References


60. LAMMPS Molecular Dynamics Simulator. at <lammps.sandia.gov>


62. The VASP Site. at <http://www.vasp.at/>

63. QUANTUM ESPRESSO. at <http://www.quantum-espresso.org/>


